Notes on an Engineering Forum
Roundtable Discussion on Permeable Reactive Walls

U.S. EPA Technical Support Project Meeting
Quality Inn
St. Petersburg, FL
February 12, 1997

S. Kinser[1] , R. L. Stamnes[1], F. Vavra[1], P. Leonard[2], S. Marquess[2],
M. Cassidy[2], R. Izraeli[3] , H. Levine[3]

WELCOME

Rich Steimle, Project Manager for EPA's Technical Support Project, welcomed all attendees to the meeting. He noted that the Technical Support Project consists of three separate forums—Ground Water, Engineering, and Federal Facilities—whose membership consists of Regional EPA technical support personnel who work to ensure consistency in the way sites are cleaned up throughout the nation. All three Forums work closely with EPA Headquarters and EPA Laboratory personnel in drafting guidance and developing issue papers on various technical topics.

ROUNDTABLE DISCUSSION ON PERMEABLE REACTIVE WALLS

Steve Kinser, Engineering Forum Co-Chair and moderator for the roundtable discussion, described the purpose for the roundtable: to identify and discuss field demonstrated permeable reactive wall materials, materials preparation and placement, and performance monitoring. He then noted that this discussion, as well as information obtained at the Containment Conference, will be used to write a technology status summary on permeable reactive walls for use by EPA project managers and permit writers. This roundtable discussion is the first in a series of roundtables the Engineering Forum intends to hold on this and other topics. The panelists then introduced themselves:

Peter Lundie, EnviroTreat, Aberdeen, Scotland
Mike Baker, University of Waterloo, Canada
Liyuan Liang, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN
John Fruchter, Battelle, Pacific Northwest National Laboratory, Richland, WA
Bob Puls, U.S. EPA, RSKERL Laboratory, Ada, OK
Timothy M. Sivavec, Corporate Research and Development Center, General Electric, Schenectady, NY
Patricia D. MacKenzie, Corporate Research and Development Center, General Electric, Niskayuna, NY
Kirk J. Cantrell, Applied Geology and Geochemistry Group, Battelle, Pacific Northwest National Laboratory, Richland, WA
George G. Teutsch, Geological Institute, University of Tübingen, Tübingen, Germany
Peter Grathwohl, Applied Geology, Geological Institute, University of Tübingen, Tübingen, Germany

Steve Kinser explained that the forums would like the panelists to first identify field-demonstrated materials that have been used in permeable reactive walls and then address different topics for each material:

---

[1]Co-Chair, Engineering Forum
[2]Co-Chair, Federal Facilities Forum
[3]Co-Chair, Ground Water Forum

The materials identified by the panel were as follows:

- Zero-Valent Iron
- Pillared Treated Clays (Organophillic Clays)
- Organic Carbon and Granular Activated Carbon
- Sodium Dithionite
- Zeolite
- Polysulfide

ZERO-VALENT IRON

[Note: Removal of chlorinated solvents with zero-valent iron is a patented process owned by the University of Waterloo.]

Materials:
Zero-valent iron is used in permeable reactive walls to primarily treat chlorinated solvents, but also has been used to treat chromate and radionuclides by reducing and precipitating inorganic chemicals. Most zero-valent iron comes from processed automobiles. It is a fairly inexpensive material that costs about $350 per ton. Some of the vendors for this material include Peerless and Master Builders. It was explained by panelists that either the material should be from one of these vendors of heat treated metal or one should proceed with caution. The heat treating process removes oil and grease which would impede the surface reactions. Panelists suggested that the following criteria should be applied when selecting zero valent iron material: 1) No toxic metals should leach out of the material. 2) The size and shape of the iron particles are important because surface area controls the rate of reactions with zero valent iron. 3) As a general rule, the material should be about size 6 mesh. 4) The material should be heat treated.

Preparation:
Zero-valent iron comes prepared for direct placement at the site and can be ordered in different size particles depending on the conditions at a particular site—for example, the residence time for contaminants to flow through the reaction cell. Zero-valent iron for the treatment of organics is a patented process and material can be ordered in sizes from 6 to 50 mesh. However, caution should be observed if an iron supplier at a site changes in the middle of the remediation. In such cases, preliminary tests should be conducted on the new iron to ensure that it will be effective at the site before it is installed.

Interferences/Incompatibilities:
There is a concern with using zero-valent iron at sites with highly-oxygenated water. Most zero-valent irons come irregularly-shaped (flakes), but one vendor makes a spherical-shaped iron, which may have less of a tendency to plug. However, it is very expensive and has not yet been tested in the field. Flake-shaped zero-valent iron can be mixed with sand to reduce the likelihood that it will plug; but in most cases, 100% iron is used. However, new, less expensive emplacement techniques will probably require mixtures. One meeting participant noted that the Elizabeth City, North Carolina, site uses 50% iron, 25% sand, and 25% aquifer material, but that the aquifer material is indigeneous to the site and may not be effective or able to be replicated in another area. Low pH can affect the effectiveness of the technology and could cause the iron to produce high hydrogen levels in the wall. Sites with high calcium carbonate waters have elevated alkalinity and salinity, which also pose precipitation problems over the long term. Sites with many shales and coals can pose a problem because the shales and coals already naturally contain polyaromatic hydrocarbons (PAHs).

Bi-metals, zero valent iron with either copper or nickel plating, were discussed. Some experiments have been run with zero valent iron that has been plated with either copper or nickel. These materials show very high rates of reaction initially, even for difficult-to-degrade compounds, such as PCBs. However, the activity of these materials degrades in the field rapidly. Nickel and copper are known to act as catalysts, but it is also known that they generally function well in "clean" environments and can be "poisoned" by compounds found in ground water. Roundtable panelists believed that the decline in the rate of reaction was due to this poisoning effect. The key point is that this material could look good in a short pilot test, but might function in the field only for a very short time.

PILLARED TREATED CLAYS

Materials:
Pillared treated clays are used to treat cations at heavy metal sites, organic material such as benzene and polynuclear aromatics, acetates, and cyanides. The cost is approximately $2,000 per ton.

Preparation:
Pillared treated clays usually arrive at the site pre-prepared, but can be prepared on site. However, the preparation of these clays is a proprietary process; therefore, an authorized vendor will need to be used.

Interferences/Incompatibilities:
Clays can be placed to a maximum depth of 50 meters using a slurry technique, but this would cost between $120 and $150 per square meter and independent of depth. [Note: Forum members are skeptical that clays can be placed to 50 meters.]

ORGANIC CARBON/GRANULAR ACTIVATED CARBON

Materials:
Organic carbon is used as a reductant to precipitate some metals. Granular activated carbon is used to adsorb PAHs and VOCs.

Preparation:
No preparation is needed for organic carbon.

SODIUM DITHIONITE AND POLYSULFIDES

[Note: These materials are not typically used in reaction walls and the Forums have seen no proven field tests for these materials.]

Materials:
Sodium dithionite and polysulfides work similarly and are used to treat chromate. Sodium dithionite costs approximately $500 per ton.

Preparation:
Sodium dithionite can be ordered as either a dry powder or dissolved wet mixture. However, the dissolved wet mixture is preferable because the dry mixture spontaneously combusts in air and could be a transportation hazard.

Interferences/Incompatibility:
Sodium dithionite and polysulfides should be injected deep into a system. This deep treatment may be able to address situations that would be impossible and/or very expensive to do with a funnel and gate system. Generally, funnel and gate systems treat ground water to a depth of 50 or 60 feet, while Sodium dithionite can be injected to much greater depths.

Zeolite

Materials:
Zeolite has absorbent and ion-exchange capabilities that can treat strontium. Research indicates that surface-modified zeolites may be able to treat cations, organics, and cyanides, but have not yet been tested in the field. They cost around $20 per ton.

Preparation:
No preparation is needed.

Performance Monitoring Considerations

A panelist noted that monitoring is needed to verify that the permeable reactive wall is working. In addition to direct monitoring of contaminants, geochemical parameters (*i.e.*, pH, Eh, and dissolved oxygen) can be measured to indicate the system's performance. Another panelist said that when she sees increased alkalinity in a wall, she will study to determine if microbial activity is occurring in the system. She then noted that a passive treatment system that has a discharge point needs to be monitored.

One panelist noted that it is difficult to do mass balance measurements in the field, but that some sites show encouraging field results with new mass balance techniques. Another panelist said that she uses monitoring as a tool for verifying the wall's performance despite the fact that monitoring is not required by regulation. This is independent of regulatory monitoring requirements that are required by CERCLA. One participant noted that Elizabeth City is only interested in results from four monitoring wells near the river at the site, but that researchers continue to monitor other areas of the site to look at the performance of the system. One panelist said that monitoring within the wall will help build some long-term performance data for these systems. Another panelist noted that monitoring funnel and gate systems versus continuous walls requires different approaches and that monitoring a funnel and gate system is easier than monitoring a continuous wall.

A panelist said that monitoring both up and down gradient of the wall is important to determine the wall's effectiveness. Another said that non-purge and passive sampling techniques should be used when sampling a permeable reactive wall. It was stated that *in situ* velocity probes are being used at a site in New Hampshire to detect correlation between the disappearance of contamination and the appearance of products. A third panelist noted that his company has had problems with these probes.

Long-Term Performance Issues

The panel noted that there are some materials that have limited breakthrough, which could affect their long-term performance. This referred to the fact that different compounds react with iron at different rates—for example TCE might be totally degraded through the wall, but PCBs, which react at a much slower rate, might only be partially degraded. The panelists also said that they have not seen a change in reactivity when using zero-valent iron over time. At the Sunnyvale Installation, where 100% zero-valent iron was used in a permeable reactive wall, the iron looked the same when it was taken out of the system as it did when it was placed two years earlier. At the Elizabeth City site, very little surface buildup was found after the wall had been in place for twenty months.

A panelist encouraged development of a database on long-term performance of permeable reactive walls in order to move this technology forward. Another panelist noted that some researchers have discussed the possibility of developing replaceable treatment cassettes for permeable reactive walls, but was not sure if these discussions were continuing. [Note: Performance of pilot scale systems has not been observed to degrade over a 2 -5 year period of operation—the actual operational lifetime of iron systems is not clearly defined and may be a function of conditions at a site. It is unclear as to the need for replacement or regeneration of iron systems in a typical system.]

DURATION

A panelist said if the residence time equals one day, then pore volume also equals one day. [Forum comment: In the case of a reactive wall, the pore volume is the effective volume of the reactor. The Forum believes the panelist meant that when the residence time equals one day, one pore volume of liquid has been processed.] Another panelist said that above-ground treatment often does not work as well as *in situ* treatment because of the potential it presents for introducing oxygen into the system. A third panelist said that models should be used to determine treatment levels, but model accuracy for field results would need to be determined first.

One Forum member asked whether the Panelists would recommend conducting both lab and pilot tests before moving permeable reactive wall technology to the field. One panelist said that she would prefer finding out more about the site—*e.g.*, whether there are increased levels of organic compounds in the site—before making that decision. She added that for a field pilot test, she would only consider conducting an *in situ* pilot to help identify costs for field applications. Another panelist said that for treating chlorinated solvents with zero-valent iron, he would recommend conducting a lab batch column test before conducting a field test. For things other than zero-valent iron, he would definitely recommend a pilot test. Long-term treatability studies are important. A third panelist noted that retrieving radionuclide waste from a system can present problems and that more work needs to be done in this area.

One Forum member asked what the long-term expectations for an underground reactive wall are and whether the reactive waste should be removed after treatment. One Panelist noted that granular-activated carbon being used to treat chlorinated solvents can be left in the ground unless there are long-term concerns. However, with metals, there are regulatory issues that will affect this decision. Another panelist noted that the decision to leave the wall in place will depend on whether precipitates were created during the reduction process. Such a scenario would also apply at a uranium site. One panelist noted that regulators will not let any material be placed underground at a uranium site unless scientists can prove that it can be retrieved.

A panelist stated that to accurately determine the operation and maintenance costs of permeable reactive walls, one would need to determine the long-term performance of the system, which is difficult to do since no data on long-term performance is available. Therefore, his company uses a best-guess estimate of 50 years. [Note: This is in contrast to another panelist who uses a five year estimate.] Conference participants did make statements that although they have noted precipitation products, they have not observed declines in the rate of reaction with zero valent iron over time. This appears to be a cause for optimism about the long term performance of these reactive walls.

One Forum member noted that there is an increasing perception among many people that reactive walls are a "permanent fix" for addressing contaminants at a site. A panelist agreed, noting that this perception started a few years back. When permeable reactive walls first evolved, they were touted as an excellent means to address dilute plumes and PRPs decided to use them instead of pump-and-treat. As time went on, they adopted the idea that once a permeable reactive wall was put into place at a site, no further work needed to be done and the contamination at the site would be taken care of. More recent experience has shown that in most cases, these permeable reactive walls will require some operation and maintenance (O&M). [Forum comment: The pH changes within the wall and, depending on the ground water chemistry, some precipitation may take place, which may form scale in the wall, thereby reducing the flow through the wall and access to the zero valent iron. Although the panelists had not so far seen any declines in the activity of the zero valent iron, if substantial scaling occurs, the rate of reaction would almost certainly decline. In some cases, treatment of the bed or replacement of the wall material may be necessary.]

A Forum member asked about the possibility of installing a reactive chamber for the permeable reactive wall above-ground. A panelist noted that to do this, the chamber would need to be very large and would require extensive structural support. In addition, it might allow unwanted *ex situ* reactions involving oxygen to occur. Another panelist added that *in situ* methods are preferable because they are more passive, result in less human exposure, require no reinjection, and enable easier reuse of the site.

One Forum member asked how one can assure that the reactive material is properly placed in the zone of interest. The panel noted that the only way to do this is to conduct monitoring and performance evaluations at the site.

COST ADVANTAGES OF PERMEABLE REACTIVE WALLS COMPARED TO PUMP-AND-TREAT

One panelist noted that when comparing costs of a funnel and gate system to pump-and-treat, the pump-and-treat system initially appears to be much less expensive; however, there are additional advantages to a funnel and gate system that make it "more economically interesting." In response to a question from a Forum member, a panelist noted that ETI assumes replacement of the wall in five years. [Note: Forum members believe that costs will be very site specific and are highly dependent on the number of times that the wall needs to be replaced. In some cases, the capital cost of a reaction wall may be less than the installation of a pump and treat system.]

OPEN DISCUSSION

One member of the audience asked the panelists if a permeable reactive wall can remediate mixed waste in a plume, specifically TCE and explosives in groundwater. One Panelist said that some research indicates that these walls can remediate TNT and RDX; remediation of TNT produces phenols, which eventually disappear. There are some compounds, however, that cannot be treated (*e.g.*, tritium).

Another member of the audience asked whether permeable reactive walls will eventually replace funnel and gate systems. One panelist said that this is unlikely since both hydrology and economic factors play a role in determining the choice of technologies used at a site. Another Panelist noted that uniformity of a wall can be assumed, but flow patterns can vary. One panelist said that a funnel and gate system would be more appropriate at a site where a faulty wall may need to be fixed. It is much easier to replace the material in the pit of a funnel and gate system than it is to excavate and replace the material in a continuous trench with the potential for wall collapse. If the water chemistry suggests fouling problems or other problems that would require periodic maintenance, a funnel and gate system may be preferred. A continuous wall may be better if one is fairly certain that the wall will not need to be replaced and the materials will treat the contamination. He then added that monitoring is easier with a funnel and gate system.

In response to a question on remediating arsenic, one Panelist noted that the University of Waterloo has used a combination of calcium and iron oxides to treat arsenic. In response to a question on particle size and plugging, a panelist said that to prevent plugging, better results can be achieved when one uses sand particles that are the same size as the iron particles in the reactive wall.

A member of the audience asked the Panelists if they had encountered problems with regulations for land disposal and mixing. A panelist noted that it is a good idea to check the state regulations to determine if the material will be considered a hazardous waste by the State; this often requires sending materials to a state-accepted test lab. A member of the audience noted that requirements may be needed for mapping the flow of the water through the reactive wall. One panelist said that his regulators require tracer tests to determine that water does <u>not</u> flow through the wall. Another panelist said that the State of North Carolina requires both compliance wells and wells to determine whether the water is moving around, through, or under the wall.